# A Novel Arsenic Cation, $[Me_2As–AsMe_2I]^+$, and the Synthesis of New Gallium–Arsenic Compounds

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The gallium halides $Ga_2X_4$ have proved to be useful reagents in the synthesis of bonds between gallium and a number of elements e.g. C [1], S and Se [2].

The importance of gallium–arsenic compounds in the semiconductor industry has prompted us to investigate analogous reactions with arsenic compounds and here describe preliminary findings.

## Synthesis of $Me_2AsGaX_2$ (X = Cl, Br, I)

Excess dry dimethylarsine was condensed on to solid $Ga_2I_4$ *in vacuo*. On stirring the mixture at 20 °C the halide slowly dissolved and hydrogen was evolved; on removal of excess dimethylarsine white powders of composition $Me_2AsGaX_2$ (X = Cl, Br, I) remained. Their vibrational spectra indicate that they are dimers probably with As bridges, similar to the S compounds previously reported [2].

*Reaction between $Me_2AsI$ and $Ga_2I_4$*

Excess dry $Me_2AsI$ was condensed on to $Ga_2I_4$ *in vacuo* and the mixture stirred rapidly at room temperature. After 2 h a yellow crystalline solid of composition $Me_4As_2GaI_5$ was deposited; satisfactory crystals for X-ray analysis were obtained by recrystallisation from benzene; other as yet unidentified Ga/As species remained in solution. $In_2I_4$ undergoes a similar reaction and $Me_4As_2InI_5$ was also isolated and we propose that this is isostructural with the gallium compound since it has almost identical vibrational spectra.

Crystal data for $Me_4As_2GaI_5$ (20°): orthorhombic, space group $P2_12_12_1$, $a$ = 14.82(1), $b$ = 12.32(1), $c$ = 10.53(1) Å. Intensity measurements were made on a Stoe STADI-2 diffractometer using Mo Kα radiation. 2082 reflections were measured and after elimination of those for which $I < 3\sigma(I)$ there remained 1375 unique reflections which were used in the final refinement. The structure which was solved using MULTAN [3] and SHELX [4], was refined anisotropically for Ga, I and As, and isotropically for C; $R$ value = 0.059. Fractional atomic coordinates are given in Table I. See also 'Supplementary Material'.

The crystal structure contains the discrete ions $[Me_2As–AsMe_2I]^+$ and $GaI_4^-$. Bond distances and angles are given in Table II; the cationic species is shown in Fig. 1 and its staggered structure in Fig. 2. The $GaI_4^-$ is approximately tetrahedral with similar

TABLE I. Fractional Atomic Coordinates (×10⁴)

| | *x* | *y* | *z* |
|---|---|---|---|
| I(1) | 1077(2) | 2760(2) | 5904(2) |
| I(2) | 4846(2) | 3968(2) | 10344(3) |
| I(3) | 4984(2) | 1345(2) | 7804(2) |
| I(4) | 4537(2) | 783(2) | 11656(2) |
| I(5) | 2532(2) | 2244(2) | 9440(3) |
| As(1) | 2307(3) | 2010(3) | 4500(4) |
| Ga | 4228(3) | 2123(3) | 9817(3) |
| As(2) | 3440(3) | 3329(3) | 3874(5) |
| C(1) | 2829(29) | 930(33) | 5447(40) |
| C(2) | 1759(27) | 1330(30) | 3056(38) |
| C(3) | 2540(36) | 4415(38) | 3305(50) |
| C(4) | 3618(33) | 3862(37) | 5680(44) |

TABLE II. Selected Bond Distances (Å) and Angles (°) in $As_2(CH_3)_4GaI_5$

| | | | |
|---|---|---|---|
| I(1)–As(1) | 2.522(4) | I(2)–Ga | 2.512(4) |
| I(3)–Ga | 2.581(5) | I(4)–Ga | 2.585(4) |
| As(1)–As(2) | 2.427(5) | I(5)–Ga | 2.550(5) |
| As(1)–C(2) | 1.916(40) | As(2)–C(3) | 1.982(51) |
| As(2)–C(4) | 2.028(47) | As(1)–C(1) | 1.833(42) |
| I(1)–As(1)–As(2) | 114.4(2) | I(1)–As(1)–C(1) | 105(1) |
| I(1)–As(1)–C(2) | 108(1) | As(2)–As(1)–C(1) | 110(1) |
| As(2)–As(1)–C(2) | 112(1) | C(1)–As(1)–C(2) | 107(2) |
| As(1)–As(2)–C(3) | 94(1) | C(3)–As(2)–C(4) | 99(2) |
| I(2)–Ga–I(3) | 111.0(2) | I(2)–Ga–I(4) | 110.4(2) |
| I(2)–Ga–I(5) | 109.9(2) | I(3)–Ga–I(4) | 107.5(2) |
| I(3)–Ga–I(5) | 108.7(2) | I(4)–Ga–I(5) | 109.2(2) |

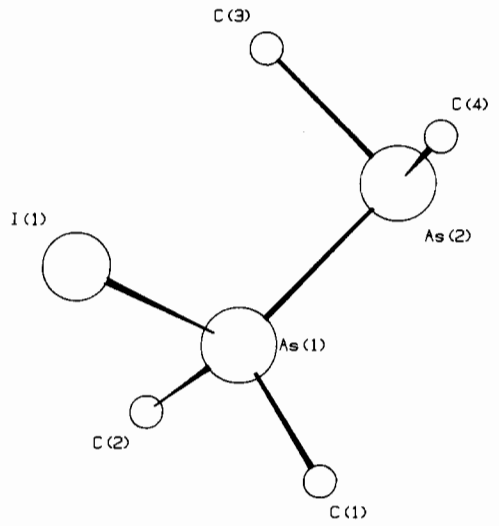


Fig. 1. The structure of $[Me_2As–AsMe_2I]^+$.

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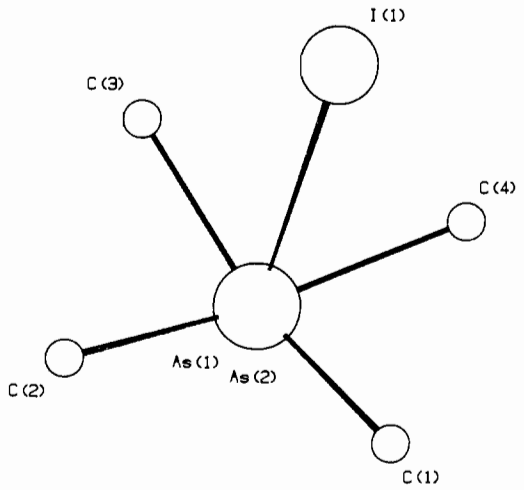


Fig. 2. View along As(1)–As(2).

bond distances and angles to those found in $Ga_2I_4$ [5]. There are no abnormal interionic distances and all bond distances lie within expected ranges.

The reaction is clearly complex; the first stage probably involves the insertion of $Ga^+$ into the As–I bond to give $Me_2As–Ga^+–I\ GaI_4^-$, followed by reaction with $Me_2AsI$ to give the As–As bonded cation.

This is the first example of an arsenic cation of this type although they have been postulated previously in the adduct dissociation in solution

$$Me_3As–AsEtCl_2 \longleftrightarrow [Me_3As–AsEtCl]^+ Cl^- \text{ [6]}.$$

## Supplementary Material

Lists of structure factors are available on request from the authors.

## References

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